Non-Aqueous Solvent-based CO_2 Capture Process

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Objective

Develop novel, non-aqueous CO_2 scrubbing solvents and capture process that substantially reduces the parasitic energy penalty and corresponding increase in cost of electricity for post-combustion CO_2 capture compared to state-of-the-art CO_2 capture processes

Performance Targets
Power Performance:
- Reboiler Duty < 2.0 GJ/tonne CO_2
- Plant Efficiency < 7 points loss

Economic Indicators:
- % Increase in COE < 50%
- Cost of CO_2 Avoided < $45/tonne

Background

Current Situation

- State-of-the-art CO_2 capture processes have high thermal and electrical energy requirements
  - Large quantity of high quality steam required for solvent regeneration → derates low-pressure steam turbine
  - Large compression energy requirement due to low CO_2 partial pressure generated during solvent regeneration → derates electrical generation
  - Parasitic power load ranges from 1,200 to 1,500 kJe / kg CO_2
- State-of-the-art CO_2 capture processes have high capital and operating costs
  - Extremely large process equipment
  - Expensive materials of construction due to corrosivity of solvents
  - High degradation rates due to O_2 and SO_2 in flue gas
  - Evaporative losses and wastewater treatment requirements
- Result
  - Increase in Cost of Electricity (ICOE): > 65%
  - Cost of CO_2 Avoided: > $60 / tonne
- Current USDOE **ICOE** targets for post-combustion CO_2 capture processes **<35%**.

Path to Reducing ICOE and Cost of CO_2 Avoided

$$ICOE\ Break\ Down[1] = \underset{Power\ Consumption}{56\%} + \underset{Capital\ Expense}{33\%} + \underset{Operating\ Expense}{11\%}$$

- Largest contributor to ICOE is the Power Consumption → Reboiler Duty
[1] Rochelle, G. T. Amine Scrubbing for CO_2 Capture. Science **2009**, 325, 1652-1654.

Reboiler Heat Duty Contribution Breakdown

$$q_R = \left[\frac{C_P(T_R - T_F)}{\Delta\alpha}\right]\frac{M_{sol}}{M_{CO_2}} + \left[\Delta H_{V,H_2O} \cdot \frac{P_{H_2O}}{P_{CO_2}} \cdot \frac{1}{M_{CO_2}}\right] + \left[\frac{\Delta H_{abs,CO_2}}{M_{CO_2}}\right]$$

Sensible Heat | Heat of Vaporization | Heat of Absorption

Solvent	C_p [J/g K]	Δh_{abs} [kJ/mol]	Δh_{vap} [kJ/mol]	X_{solv} [mol solvent/ mol solution]	$\Delta\alpha$ [mol CO_2/ mol solvent]	Reboiler Heat Duty [GJ/tonne CO_2]
MEA (30%)	3.8	85	40	0.11	0.34	3.22
Lower Energy Solvent System	↓	↓	↓	↑	↑	↓

- Aqueous systems have similar properties such as high heat capacities, heats of absorption and vaporization, and high dilutions
- Reboiler heat duties are similar and can only be *improved marginally* by lower heats of absorption or increase in concentration of amine.
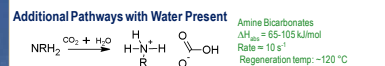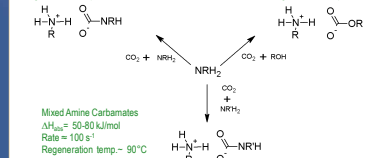
Development Approach

Non-aqueous solvent systems
- Desirable physical and chemical properties to lower reboiler duty
- Multiple reaction pathways

Potential Pathways for CO_2 Capture in Non-Aqueous Solvents

Amine Carbamates
ΔH_{abs} = 50-95 kJ/mol
Rate = 10,000 s⁻¹
Regeneration temp: ~120 °C

Carbonate Esters
ΔH_{abs} = 50-80 kJ/mol
Rate = not determined
Regeneration temp: ~ 90°C

Mixed Amine Carbamates
ΔH_{abs} = 50-80 kJ/mol
Rate = 100 s⁻¹
Regeneration temp: ~ 90°C

Additional Pathways with Water Present

Amine Bicarbonates
ΔH_{abs} = 65-105 kJ/mol
Rate = 10 s⁻¹
Regeneration temp: ~120 °C

Development Approach (cont'd)

Technical Challenges for Non-Aqueous Solvents

- Chemical degradation by water
  - Water reacts with stronger bases producing the hydroxide anion
  - CO_2 is absorbed as a bicarbonate salt requiring more energy for regeneration
- Physical accumulation of water from flue gas in solvent
  - Flue gas from wet FGD is saturated (~15%) with water vapor
  - Water can condense or be desiccated by non-aqueous solvents in the absorber vessel under optimal absorption conditions until VLLE is established
- Solids formation in rich solvent
  - Many non-aqueous solvents form insoluble solids at high CO_2 loadings
  - Solids can accumulate in packing or other undesirable areas in the process
- Viscosity of solvent
  - Affects rate of CO_2 capture and operation of columns
  - Impacts size of absorber and regenerator vessels
- Foaming
  - Many aqueous and non-aqueous solvents foam when purged with gases
  - Anti-foaming agents must be added to avoid entrainment and frothing

Development approach is focused on addressing these and additional challenges
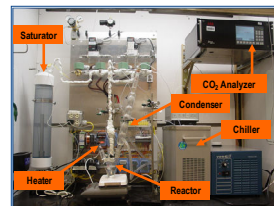
Technology Development Plan
Transitioning from novel solvent concept to commercial

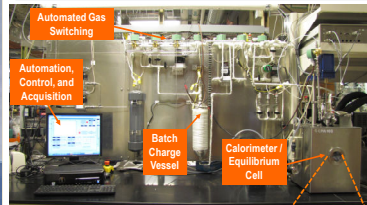|	Previous Work	Current Project	Future Development		
Yr	2009-10	2010-13	2014-15	2016-18	2019+
TRL	1 2 3	4	5	6 7	8 9

Proof of Concept/Feasibility
Prototype Testing at Power Plant

Laboratory Validation
- Comprehensive solvent screening
  - Identify solvent systems
  - Determine thermodynamic and physico-chemical properties for novel systems
- CO_2 capture process modeling
  - Develop comprehensive process model
  - Evaluate novel process configurations and integration schemes
  - Compare performance with conventional solvent systems

Relevant Environment Validation
- Bench-scale testing to assess solvent performance
  - Continuous flow CO_2 capture unit
  - Long term (1,000 hours) stability testing with high-fidelity flue gas
  - Collect process data to support simulation and design of pilot unit de
- CO_2 capture process modeling
  - Update process models
  - Technical and economic assessment

Experimental Resources

Highly Automated Solvent Evaluation System

Saturator, CO_2 Analyzer, Condenser, Chiller, Heater, Reactor

Fully-automated VLE and Reaction Calorimeter

Automated Gas Switching; Automation, Control, and Acquisition; Batch Charge Vessel; Calorimeter / Equilibrium Cell
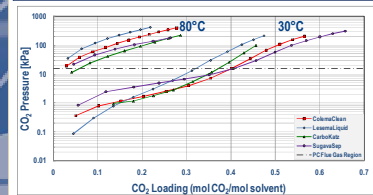
Capabilities
- Vapor-liquid Equilibrium (P_{CO_2} vs CO_2 Loading)
- Reaction Calorimetry (Heat of CO_2 Absorption)
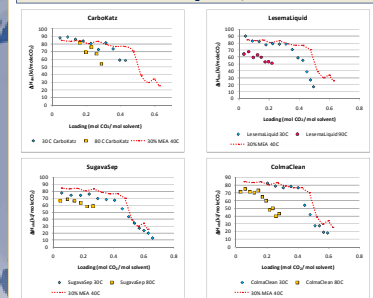- Specific Heat Capacity
- Vapor Pressure

Experimental Results

Early Findings on Novel Non-aqueous CO_2 Solvents

Advantages
- High CO_2 loading capacities
- Low regeneration temperatures
- Not degraded by water
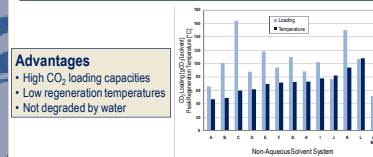
CO_2 Vapor-Liquid Equilibrium

Heat of CO_2 Absorption

CarboKatz, LesemaLiquid, SugavaSep, ColmaClean

Long-Term Testing with High-fidelity Flue Gas

Evaluation Conditions

Absorption:
- Temperature: 30°C
- Flue Gas Composition: 14%CO_2, 4%O_2, 50 ppm SO_2, Bal. N_2
- Water Content: Solvent fully saturated

Regeneration:
- Temperature: Ramp to 75°C
- Gas Composition: N_2 Purge
- Water Content: Solvent fully saturated

Solvents evaluated continuously for ~400 hours
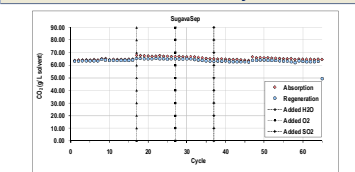
### Water accumulation is a major hurdle for non-aqueous systems

RTI's Non-Aqueous Solvents:
- Are selective for non-aqueous reaction pathways in the presence of water
- Have low water solubility and therefore form a separate liquid phase in the presence of water
- Maintain a system-wide water balance without distillation and offer low-energy separation options
- Have low regeneration temperatures allowing use of lower quality steam

Phase Separation
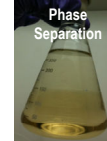
Process Engineering

Estimate Reboiler Heat Duty using Short-cut Method[2]

[2] Notz et al. A short-cut method for assessing absorbents for post-combustion carbon dioxide capture. International Journal of Greenhouse Gas Control **2011**, 5, 3 413-421.
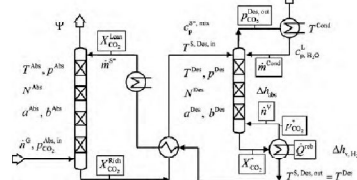
*Boxed parameters are calculated

- Short-cut method for estimating the reboiler duty is a very useful tool for identifying promising solvent systems
  - Uses experimentally collected data (no inferred or estimated properties)
  - Has been shown to accurately estimate the reboiler duty (largest contributor to the total energy penalty)
  - Approach is fundamentally applicable to all gas absorption systems
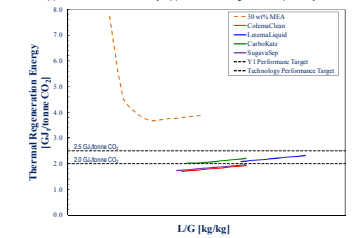
Conditions:
- CO_2 Capture Extent: 90 %
- CO_2 Absorber Temperature: 40°C
- Crossover Temp. Approach: 10°C
- Regenerator Temperature: 120°C
- Regenerator Pressure: 2000 mbar

Results:
- Non-aqueous solvents have regeneration energies < 2.5 GJ/tonne CO_2
- > 35 – 55 % reduction compared to SOTA processes

- Process model of a supercritical PC power plant has been developed to estimate parasitic power load and net energy penalty (Aspen Plus)
  - Basis: Case 12 – Supercritical PC Power Plant with CO_2 Capture. Cost and Performance Comparison of Fossil Energy Power Plants (2007), DOE/NETL-2007/1281.

Case 12 – Supercritical PC Power Plant				
Constant Coal Feed Rate [2,005,660kWt]				
CO_2 Capture Scenario	Net Power [kWe]	Net Efficiency [%]	Efficiency Point Loss	Parasitic Power Load[1] [kJe/kg CO_2]
No Capture	784,700	39.1	-	N/A
With Capture Econamine FG+	545,995	27.2	11.9	1,511
Non-Aqueous Solvents				
CarboKatz	643,585	32.1	7.0	900
SugavaSep	672,729	33.6	5.5	710
ColemaClean	642,788	32.1	7.0	900
LesemaLiquid	631,385	31.5	7.6	970

- Non-Aqueous solvent CO_2 capture processes have much lower parasitic power loads
  - Primarily due to lower quantity and quality of steam required for solvent regeneration
- Parasitic power load [kJe / kg CO_2] of non-aqueous solvents is approx. 50% of state-of-the-art CO_2 capture processes
- Potential for significant reduction in increase in cost of electricity

Current and Planned Activities

- Design and construction of a bench-scale process unit for evaluating non-aqueous solvents in a representative process configuration, under realistic conditions with real, fossil fuel derived flue gas
  - Installed, commissioned, and operational by January 2012
- Long-term evaluation of non-aqueous solvents with real flue gas
- Continued detailed technical and economic assessment